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AA613 AA615 AA629 AA67X AA671 AA673 AA675
AA677 AA679 AA68X AA681 AA683 AA685 AA687
AA689 AA69X AA693 AA695 AA696 AA699 AA70X
A712
U1S S1851

(56) Documents Cited

EP 0014335 A1 JP 010205061 A US 4018576 A
US 3188203 A

(58) Field of Search

UK CL (Edition R) C7A
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Online: PAJ, WPI

(54) Abstract Title

Nickel-based brazing alloys

(57) A first brazing filler metal is composed of 20-30 wt% Cr, 3-10 wt% P, 2-7 wt% Si, and remainder Ni. It may be incorporated with another brazing filler metal composed of 10-15 wt% Cr, 7-12 wt% P, and the remainder Ni in an amount of 2-15 wt%. A second brazing filler metal is composed of 18.5-29.7 wt% Cr, 3.1-10.3 wt% P, 1.7-6.9 wt% Si, and the remainder Ni. The present invention also provides an exhaust gas recirculation system cooler brazed with any of the above brazing filler metals.

GB 2 347 939 A

At least one drawing originally filed was informal and the print reproduced here is taken from a later filed formal copy.

TEST FOR RESISTANCE TO CORROSION BY SULFURIC ACID

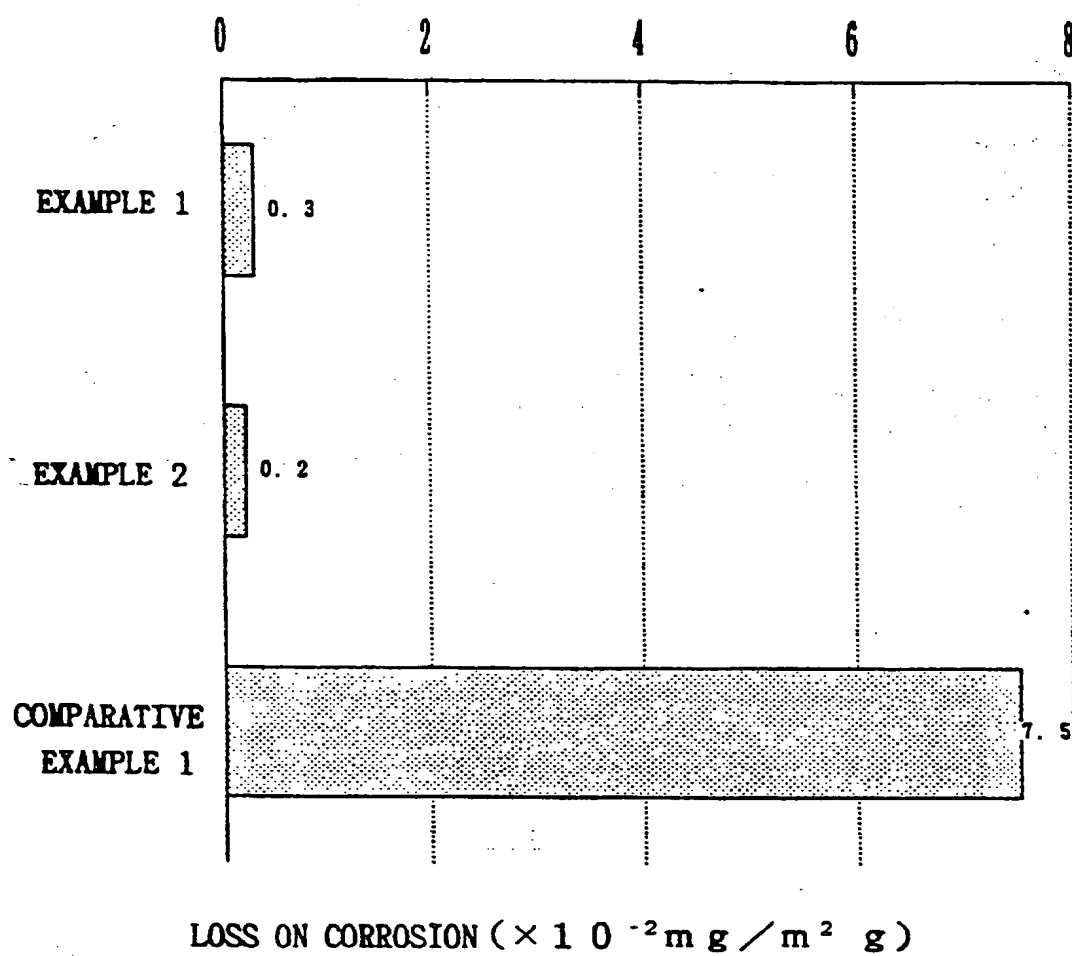


Fig. 1

Fig. 2 (a)

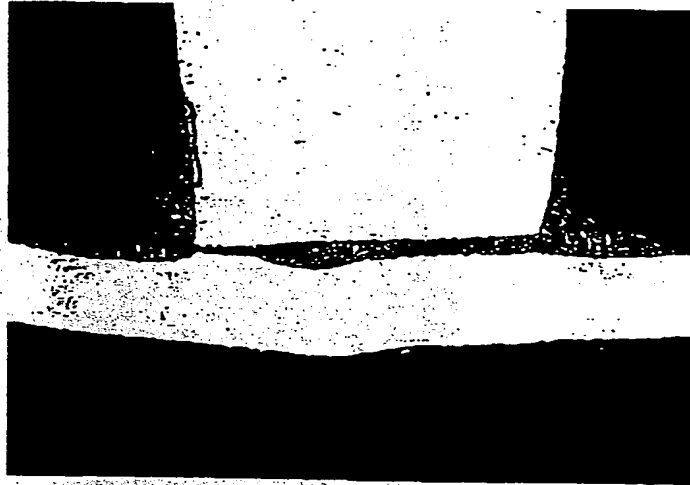


Fig. 2 (b)

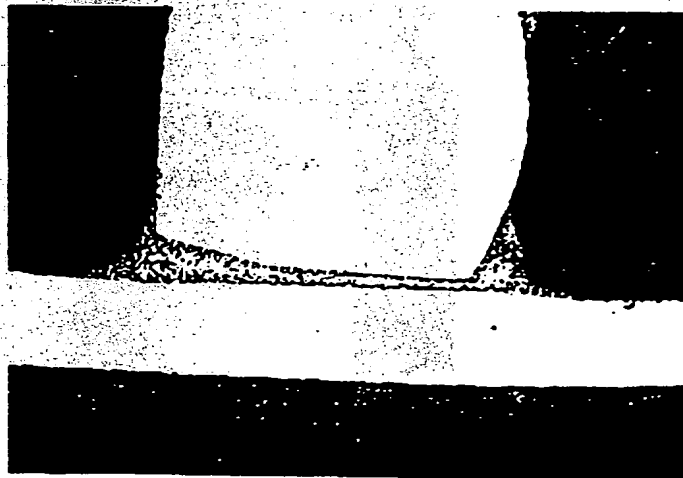


Fig. 2 (c)



Fig. 3 (a)

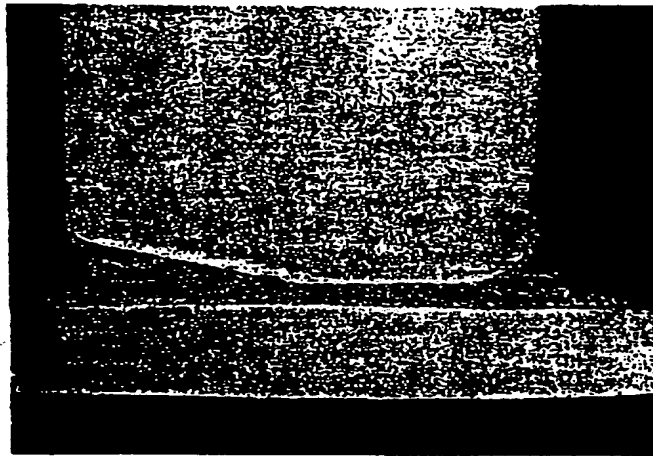


Fig. 3 (b)

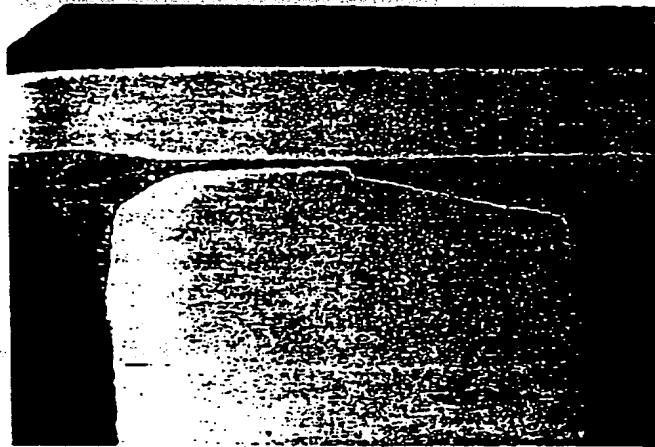


Fig. 3 (c)

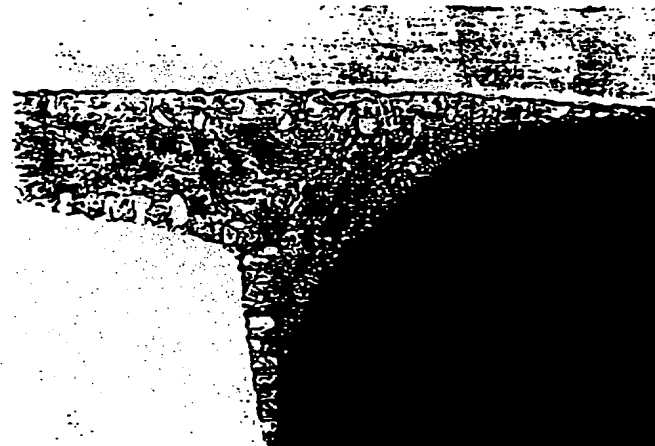


Fig. 4 (a)



Fig. 4 (b)

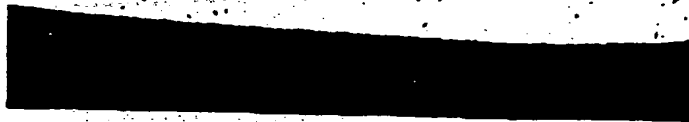
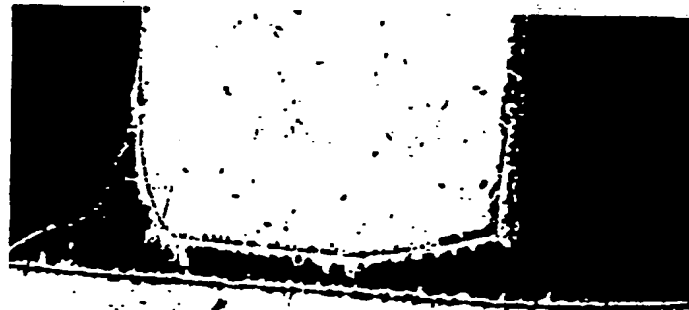
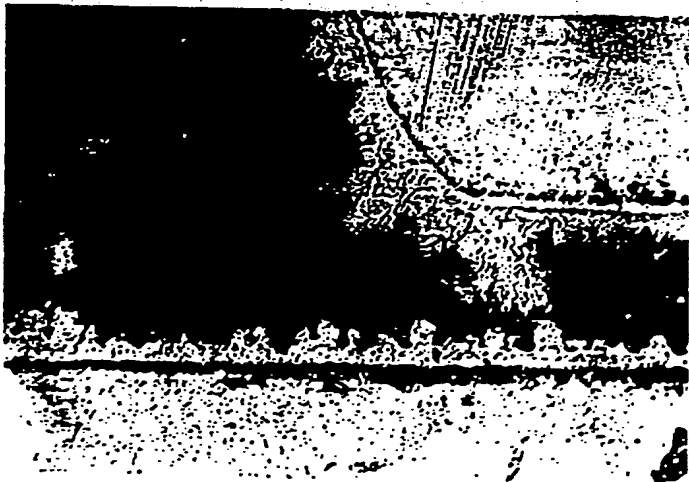
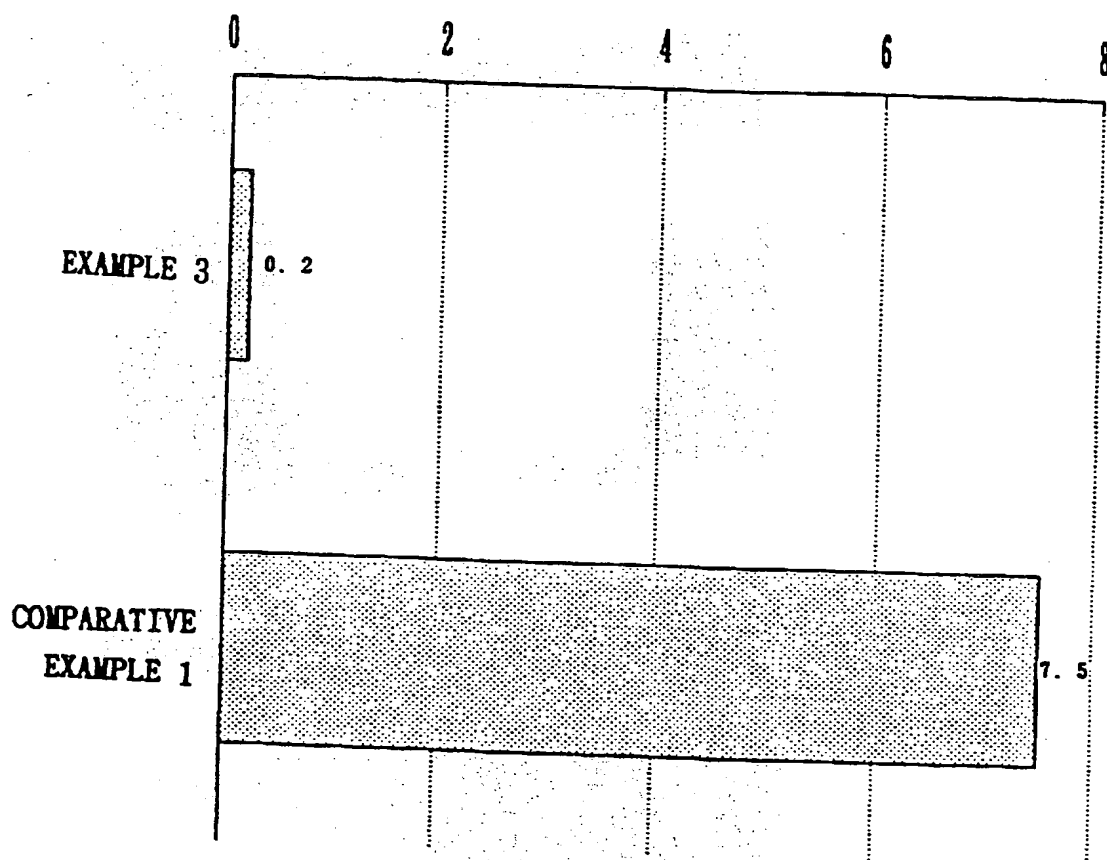


Fig. 4 (c)



TEST FOR RESISTANCE TO CORROSION BY SULFURIC ACID



LOSS ON CORROSION ($\times 10^{-2} \text{ mg/m}^2 \text{ g}$)

Fig. 5

Fig. 6 (a)

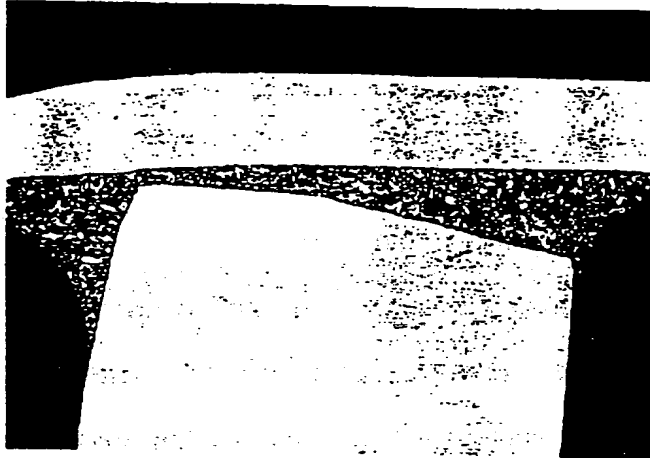


Fig. 6 (b)



Fig. 6 (c)



BRAZING FILLER METAL SUPERIOR IN CORROSION RESISTANCE AND HEAT RESISTANCE, AND EGR COOLER BRAZED WITH SAID BRAZING FILLER METAL

BACKGROUND OF THE INVENTION

1. Field of the Invention:

The present invention relates to a brazing filler metal superior in corrosion resistance and heat resistance. More particularly, the present invention relates to a brazing filler metal superior in resistance to corrosion by sulfuric acid, which is used for a component of the EGR system (such as EGR cooler). The present invention relates also to an EGR cooler brazed with said brazing filler metal.

2. Description of the Prior Art:

Among components requiring high corrosion resistance and heat resistance is that of the EGR (Exhaust Gas Recirculation) system. This system is designed to take out part of exhaust gas from the exhaust system and return it to the induction system of the engine, thereby adding it to mixture. EGR is effective in suppressing the formation of nitrogen oxides, reducing the pumping loss, decreasing the temperature of combustion gas, thereby reducing radiation heat which escapes to the coolant, and increasing the specific heat due to change in amount and composition of the working gas, thereby improving the cycling efficiency. Therefore, it is regarded as an

effective means to improve the thermal efficiency of an engine while purifying exhaust gas.

The EGR system mentioned above consists of such components as EGR pipe and EGR valve. Unfortunately, the EGR valve is subject to thermal deterioration (leading to early breakage) as the EGR gas increases in temperature and volume. Coping with this needs a water-cooled structure. In addition, EGR increases the intake temperature and hence decreases the charging efficiency, which leads to a decrease in fuel efficiency. In order to get around these difficulties, there has been developed a cooled EGR system which is so designed as to cool EGR gas with the engine coolant. The cooled EGR system is equipped with an EGR cooler which is a multi-tubular heat exchanger made of austenitic stainless steel (Japanese Patent Laid-open No. 89491/1997) or a plate-type heat exchanger (Japanese Patent Laid-open No. 89880/1998).

Meanwhile, the component (particularly the EGR cooler) of the cooled EGR system is assembled conventionally by brazing with a brazing filler metal designated as BNi-5 in JIS Z3265. BNi-5 is composed of Cr (18-19 wt%), Si (9.5-10.5 wt%), B (0.03 wt% or less), C (0.10 wt% or less), P (0.02 wt% or less), and Ni (remainder). This brazing filler material, however, suffers the disadvantage of having a high melting point of about 1080 to 1135°C. It needs a brazing temperature as high as 1150-1205°C. Brazing at such a high temperature deteriorates

the base metal and also produces an adverse effect on corrosion resistance due to precipitation of chromium carbide. This created demand for a brazing filler metal capable of brazing at a lower temperature than before. This demand has been met by the one designated as BNi-2 in JIS Z3265. BNi-2 is composed of Cr (6.0-8.0 wt%), B (2.75-3.50 wt%), Si (4.0-5.0 wt%), Fe (2.5-3.5 wt%), C (0.06 wt% or less), P (0.02 wt% or less), and Ni (remainder). It has a melting point of about 970-1000°C and is capable of brazing at 1010-1175°C.

BNi-2 is still unsatisfactory because it is poor in resistance to sulfuric acid. Exhaust gas being circulated in the EGR system condenses upon cooling, and the resulting condensate contains sulfuric acid which causes corrosion to the brazing filler metal itself and its diffused part.

Among brazing filler metals specified in JIS Z3265, BNi-7 is the lowest in melting point. It is composed of Cr (13.0-15.0 wt%), B (0.01 wt% or less), Si (0.10 wt% or less), Fe (0.20 wt% or less), C (0.08 wt% or less), P (9.7-10.5 wt%), and Ni (remainder). It has a melting point of 890°C, which is lower than that of BNi-2; however, it is poor in resistance to corrosion by sulfuric acid.

SUMMARY OF THE INVENTION

The first object of the present invention is to provide a brazing filler metal and a durable EGR cooler brazed with it. Like BNi-2 mentioned above, this brazing filler metal is

capable of brazing at 1060-1120°C. It protects the base metal from degradation and improves its corrosion resistance. It has high strength. It exhibits good corrosion resistance and heat resistance (particularly resistance to oxidation and corrosion by sulfuric acid). It also exhibits good wetting characteristics.

The second object of the present invention is to provide a brazing filler metal and a durable EGR cooler brazed with it. This brazing filler metal has a melting point of 890-980°C and is capable of brazing at 1100°C or below. (The melting point is close to that of BNi-7, and the brazing temperature is lower than that of BNi-2 mentioned above). It protects the base metal from degradation and improves its corrosion resistance. It has high strength. It exhibits good corrosion resistance and heat resistance (particularly resistance to oxidation and corrosion by sulfuric acid). It also exhibits good wetting characteristics.

The first object mentioned above is achieved by the first embodiment of the present invention. The first embodiment is concerned with a brazing filler metal superior in corrosion resistance and heat resistance which is composed of Cr (20-30 wt%), P (3-10 wt%), Si (2-7 wt%), and Ni (remainder). The brazing filler metal may be incorporated with another brazing filler metal composed of Cr (10-15 wt%), P (7-12 wt%), and Ni (remainder) in an amount of 2-15 wt%. The first embodiment

is concerned also with an EGR cooler brazed with said brazing filler metal.

The second object mentioned above is achieved by the second embodiment of the present invention. The second embodiment is concerned with a brazing filler metal superior in corrosion resistance and heat resistance which is composed of Cr (18.5-29.7 wt%), P (3.1-10.3 wt%), Si (1.7-6.9 wt%), and Ni (remainder). The second embodiment is concerned also with an EGR cooler brazed with said brazing filler metal.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a graph showing the result of test for resistance to corrosion by 5% sulfuric acid in Examples 1 and 2 (both pertaining to the first embodiment) and Comparative Example 1.

Figs. 2(a) to 2(c) are microphotographs showing the metal structure of the brazed part obtained in Example 1. Fig. 2(a) is the one (x38) taken before corrosion test. Fig. 2(b) is the one (x38) taken after corrosion test. Fig. 2(c) is an enlarged one (x100) of Fig. 2(b).

Figs. 3(a) to 3(c) are microphotographs showing the metal structure of the brazed part obtained in Example 2. Fig. 3(a) is the one (x38) taken before corrosion test. Fig. 3(b) is the one (x38) taken after corrosion test. Fig. 3(c) is an enlarged one (x100) of Fig. 3(b).

Figs. 4(a) to 4(c) are microphotographs showing the metal

structure of the brazed part obtained in Comparative Example 1. Fig. 4(a) is the one ($\times 38$) taken before corrosion test. Fig. 4(b) is the one ($\times 38$) taken after corrosion test. Fig. 4(c) is an enlarged one ($\times 100$) of Fig. 4(b).

Fig. 5 is a graph showing the result of test for resistance to corrosion by 5% sulfuric acid in Example 3 (pertaining to the second embodiment) and Comparative Example 1.

Figs. 6(a) to 6(c) are microphotographs showing the metal structure of the brazed part obtained in Example 3. Fig. 6(a) is the one ($\times 38$) taken before corrosion test. Fig. 6(b) is the one ($\times 38$) taken after corrosion test. Fig. 6(c) is an enlarged one ($\times 100$) of Fig. 6(b).

DETAILED DESCRIPTION OF THE INVENTION

The first embodiment of the present invention is concerned with a brazing filler metal composed of Cr (20-30 wt%), P (3-10 wt%), Si (2-7 wt%), and Ni (remainder). The function of each component is explained below.

Cr contributes to resistance to corrosion by sulfuric acid. With a Cr content more than 30 wt%, the brazing filler metal has such a high melting point that it causes the base metal to deteriorate in quality or decrease in corrosion resistance and it prevents continuous brazing operation in a furnace and hence aggravates productivity. With a Cr content less than 20 wt%, the brazing filler metal is poor in resistance to corrosion by sulfuric acid and hence it cannot be applied

to EGR coolers which need durability.

P decreases the melting point of the brazing filler metal. With a P content more than 10 wt% or less than 3 wt%, the brazing filler metal has such a high melting point that it causes the base metal to deteriorate in quality or decrease in corrosion resistance.

Si increases the strength of the brazing filler metal. With an Si content more than 7 wt%, the brazing filler metal is brittle and subject to oxidation. With an Si content less than 2 wt%, the brazing filler metal is poor in strength and subject to cracking (after brazing).

The brazing filler metal according to the first embodiment of the present invention is characterized by its low melting point of 970-1080°C (and hence low brazing temperature of 1060-1120°C) which is realized without loss in brazing strength.

The present invention also covers another brazing filler metal which is obtained by incorporating the above-mentioned brazing filler metal (referred to as the first brazing filler metal) with 2-15 wt% of the second brazing filler metal which is composed of Cr (10-15 wt%), P (7-12 wt%), and Ni (remainder).

The second brazing filler metal suppresses oxidation of the first brazing metal and improves wetting characteristics of the first brazing filler metal. It lowers the melting point of the combined brazing filler metal by about 100°C to 890-980°C

(permitting brazing operation at 950-1050°C). The amount of the second brazing filler metal should be 2-15 wt% to prevent an occurrence of erosion and corrosion to the base metal. With an amount less than 2 wt%, the second brazing filler metal does not produce the above-mentioned effect (or suppression of oxidation and wetting characteristics). With an amount more than 15 wt%, the second brazing filler metal causes erosion and corrosion to the base metal.

Cr in the second brazing filler metal improves the first brazing filler metal in resistance to corrosion by sulfuric acid. With an amount more than 15 wt%, Cr increases the melting point, causing the base metal to deteriorate in quality and to decrease in corrosion resistance. With an amount less than 10 wt%, Cr causes the combined brazing filler metal to decrease in resistance to corrosion by sulfuric acid.

P in the second brazing filler metal lowers the melting point and improves the wetting characteristics. With an amount more than 12 wt% or less than 7 wt%, P does not produce the above-mentioned effect.

The first and second brazing filler metals may be used in any of the following manners.

- (a) Mix them together in the form of powder.
- (b) Mix them together in the form of paste.
- (c) Place them one over the other in the form of paste or foil.

In the third manner, the lower layer should be formed from the first brazing filler metal and the upper layer should be formed from the second brazing filler metal. This arrangement permits the upper layer (of the second brazing filler metal having a lower melting point) to melt first, covering the lower layer (of the first brazing filler metal).

The brazing filler metal pertaining to the first embodiment of the present invention is applied to multi-tubular EGR coolers or plate-type EGR coolers.

Multi-tubular EGR coolers have heat-exchanger tubes made of austenitic stainless steel, such as SUS304, SUS304L, SUS316, SUS316L, and SUS321. These tubes are 6.35 mm or 5.00 mm in outside diameter and 120-600 mm in length. (The lengths are not specifically restricted.) The shell and tube sheet may be made of the same material as mentioned above or may be casting of SCS corresponding to the above-mentioned material.

In the case of plate-type EGR coolers, their flat plate or corrugated plate may also be made of the same material as mentioned above.

The brazing filler metal according to the second embodiment of the present invention is composed of Cr (18.5-29.7 wt%), P (3.1-10.3 wt%), Si (1.7-6.9 wt%), and Ni (remainder). The function of each component is explained below.

Cr contributes to resistance to corrosion by sulfuric

acid. With a Cr content more than 29.7 wt%, the brazing filler metal does not permit brazing operation at temperatures lower than 1100°C. Brazing at high temperatures causes the base metal to deteriorate in quality and corrosion resistance. It also prevents continuous brazing operation in a furnace and hence aggravates productivity. With a Cr content less than 18.9 wt%, the brazing filler metal is poor in resistance to corrosion by sulfuric acid and hence it cannot be applied to EGR coolers which need durability.

P decreases the melting point of the brazing filler metal. With a P content more than 10.3 wt% or less than 3.1 wt%, the brazing filler metal does not permit brazing operation at 1100°C or below and brazing at high temperatures causes the base metal to deteriorate in quality and corrosion resistance.

Si increases the strength of the brazing filler metal. With an Si content more than 6.9 wt%, the brazing filler metal is brittle and subject to oxidation. With an Si content less than 1.7 wt%, the brazing filler metal is poor in strength and subject to cracking (after brazing).

The brazing filler metal pertaining to the second embodiment of the present invention has a melting point as low as 890-980°C and hence permits brazing to be carried out at 950-1050°C with improved wetting characteristics, without impairing brazing strength.

The brazing filler metal of the present invention can

be used in the form of powder, paste, foil, or sheet when it is applied to the brazing part. In addition, it can be used at a low brazing temperature and hence it permits continuous brazing operation in a furnace with a reducing atmosphere.

The aforesaid brazing filler metal pertaining to the second embodiment of the present invention is used for the brazing of multi-tubular EGR coolers and plate-type EGR coolers.

As to the material and dimensions of the components of the multi-tubular EGR coolers or as to the flat plate and corrugated plate of the plate-type EGR coolers, the same explanation as mentioned above in the first embodiment is applicable.

EXAMPLES

The invention will be described with reference to the following Examples and Comparative Examples.

Example 1

A brazing filler metal specified below was used to braze a multi-tubular EGR cooler (for a diesel car) which consists of precision-cast end caps (made of SCS13), tube sheet, shell, and heat-exchanger tubes (made of SUS304). The shell holds 30 heat-exchanger tubes, each measuring 6.35 mm in outside diameter and 250 mm long.

Cr : 25 wt%, P : 8 wt%, Si : 6 wt%, Ni : remainder.

The brazing filler metal (in the form of powder) was mixed with

a binder to be made into a paste. Brazing was carried out continuously in a furnace of hydrogen atmosphere at 1100°C. The EGR cooler obtained by brazing in this manner was tested for resistance to corrosion by 5% sulfuric acid as follows.

Sulfuric acid: 5 wt% (diluted with distilled water)

Solution temperature: 80°C

Method: immersion in solution (with stirring)

Judgment: by measurement of loss on corrosion after immersion for 24 hours

The results of the test are shown in Figs. 1 and 2.

It is noted from Figs. 1 and 2 that very little corrosion occurred in the brazing filler metal and the base metal into which the brazing filler metal had diffused. It is concluded that the brazing filler metal in this example is superior in resistance to corrosion by sulfuric acid.

Example 2

Brazing with two kinds of brazing filler metals (both in paste form) was performed as follows on the same EGR cooler as used in Example 1. A first brazing filler metal is the same one as in Example 1. A second brazing filler metal is composed of Cr (12 wt%), P (8 wt%), and Ni (remainder). They were applied sequentially in two layers. The ratio of the first one to the second one is 90:10 in wt%. Brazing was carried out continuously in a furnace of hydrogen atmosphere at 1100°C. The EGR cooler obtained by brazing in this manner was tested

for resistance to corrosion by 5% sulfuric acid in the same way as in Example 1. The results are shown in Figs. 1 and 3.

It is noted from Figs. 1 and 3 that very little corrosion occurred in the brazing filler metal and the base metal into which the brazing filler metal had diffused. It is concluded that the brazing filler metal in this example is superior in resistance to corrosion by sulfuric acid.

Comparative Example 1

Brazing with a brazing filler metal of the following composition was performed as follows on the same EGR cooler as used in Example 1.

Cr (7 wt%), B (3 wt%), Si (4 wt%), Fe (3 wt%), Ni (remainder)
(This brazing filler metal is that designated as BNi-2 in JIS Z3265.) After mixing with a binder, the brazing filler metal in paste form was used for continuous brazing at 1070°C in a furnace of hydrogen atmosphere.

The EGR cooler obtained by brazing in this manner was tested for resistance to corrosion by 5% sulfuric acid in the same way as in Example 1. The results are shown in Figs. 1 and 4.

It is noted from Figs. 1 and 4 that corrosion occurred in the brazing filler metal and the base metal into which the brazing filler metal had diffused. This corrosion is due to boron which has diffused into the base metal.

Example 3

Brazing with a brazing filler metal of the following

composition was performed as follows on the same EGR cooler as used in Example 1.

Cr (23.8 wt%), P (7.3 wt%), Si (4.5 wt%), Ni (remainder)
(This brazing filler metal has a melting point of 890-950°C.)
After mixing with a binder, the brazing filler metal in paste form was used for continuous brazing at 1040°C in a furnace of hydrogen atmosphere.

The EGR cooler obtained by brazing in this manner was tested for resistance to corrosion by 5% sulfuric acid in the same way as in Example 1. The results are shown in Figs. 5 and 6. (Incidentally, Fig. 5 is compared with the result in Comparative Example 1 to facilitate understanding.)

It is noted from Figs. 5 and 6 that very little corrosion occurred in the brazing filler metal and the base metal into which the brazing filler metal had diffused. It is concluded that the brazing filler metal in this example is superior in resistance to corrosion by sulfuric acid.

As mentioned above, the brazing filler metal of the present invention permits brazing at 1060-1120°C which is close to the brazing temperature of BNi-2 specified in JIS Z3265. Also, the brazing filler metal of the present invention has a melting point of 890-980°C which is close to that of BNi-7 and permits brazing at a temperature lower than 1000°C. Therefore, the brazing filler metal of the present invention improves the base metal in corrosion resistance without

deterioration. In addition, it has good resistance to oxidation and good resistance to corrosion by sulfuric acid. It has high strength, good heat resistance, and good wetting characteristics. It is used to produce durable EGR coolers by brazing.



INVESTOR IN PEOPLE

Application No: GB 0001583.4
Claims searched: 1-5

17

Examiner: Matthew Lawson
Date of search: 11 July 2000

Patents Act 1977 Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.R): C7A

Int Cl (Ed.7): B23K, C22C

Other: Online: PAJ, WPI

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
X	EP 0014335 A1 (ALLIED) - the whole specification, especially claim 4.	1-5
X	JP 010205061 A (MITSUBISHI) - alloys 11 & 12 in the table and PAJ vol. 013, no. 510.	1-5
X	US 4018576 (LOWDER) - claim 1.	1,2 & 4
X	US 3188203 (PEASLEE) - the whole specification, especially claim 1.	1-5

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.



INVESTOR IN PEOPLE

Application No: GB 0001583.4
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Patents Act 1977 Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.R): C7A

Int Cl (Ed.7): B23K, C22C

Other: Online: PAJ, WPI

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
X	EP 0014335 A1 (ALLIED) - the whole specification, especially claim 4.	1-5
X	JP 010205061 A (MITSUBISHI) - alloys 11 & 12 in the table and PAJ vol. 013, no. 510.	1-5
X	US 4018576 (LOWDER) - claim 1.	1,2 & 4
X	US 3188203 (PEASLEE) - the whole specification, especially claim 1.	1-5

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.